

Gaseous Losses of Nitrogen other than through Denitrification

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Nitrogen losses from human activities are the major reason behind the growing concerns about the enrichment of the biosphere with reactive N, and crop production is by far the single largest cause of human alteration of the global N cycle (Smil, 1999). Effects of N enrichment range from atmospheric changes to alterations of terrestrial and aquatic ecosystems. Reactive atmospheric N trace gases resulting from agricultural activities include NO_x (NO and NO_2), NH_x (NH_3 and NH_4^+), and N_2O . An accurate quantification of sources and sinks for reactive atmospheric N trace gases constitutes a considerable scientific challenge because of large temporal and spatial variability.

Ammonia (NH_3) is the dominant alkaline gas in the atmosphere. It readily reacts with atmospheric acids to form NH_4^+ that is an important constituent in aerosols and in precipitation (Schjoerring et al., 1993). Dentener and Crutzen (1994) reported that atmospheric aerosols, acting as cloud condensation nuclei, consist in great part as sulfate neutralized to various degrees by NH_3 . Ammonia gas is predominantly removed from the atmosphere by dry deposition, while NH_4^+ aerosols are removed mainly by wet deposition (Asman and Janssen, 1987).

After being deposited, NH_3 and NH_4^+ may have serious ecological and environmental effects (Schjoerring et al., 1993). The deposition of NH_3 and NH_4^+ may contribute to soil acidification, eutrophication, foliar leaching of nutrients and increased plant sensitivity to other stress factors such as ozone, drought, frost, and fungal diseases (Yamulki et al., 1996). Nitrification of deposited NH_3 and NH_4^+ enhances the acidification of forest soils as well as the acidification of ecosystems such as heathlands and freshwater lakes (Schjoerring et al., 1993). Deposition of NH_3 and NH_4^+ to N-deficient terrestrial ecosystems represents a major perturbation to ecosystem stability and biodiversity: fertilizing plants with N from the atmosphere initiates changes in the competitive relations among plant species, so

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that slow-growing plant species are replaced by fast-growing grass species benefiting from the N enrichment (Heil and Bruggink, 1987). In aquatic ecosystems, deposition of NH_3 and NH_4^+ contributes to eutrophication, which may lead to algal blooming with subsequent fish kills (Schjoerring et al., 1993).

Major sources of atmospheric NH_3 include volatilization from decomposition of animal excrement, fertilized and unfertilized soils, vegetation, oceans, biomass burning, and other combustion processes (Dentener and Crutzen, 1994). Ammonia can be either deposited to soils and plants or emitted from soils and plants (Yamulki et al., 1996). The bidirectional nature of NH_3 exchange has made the extrapolation of NH_3 fluxes from short periods of measurements to annual net fluxes a speculative exercise. Also, the large spatial variability in ambient NH_3 concentration and land use further complicates the interpolation of NH_3 fluxes to landscape scales (Fowler et al., 1998).

Gaseous nitrogen oxides are produced in several ecosystem processes and in turn have a number of critical influences on the chemistry and physics of the atmosphere. For example, nitrous oxide (N_2O) is radiatively active and thus an important "greenhouse" gas. In the troposphere, N_2O has a lifetime of about 120 yr and this long persistence permits transport to the stratosphere where it ultimately is destroyed by photolysis (Liu et al., 1999). This photolytic reaction catalyzes a set of reactions that result in the destruction of stratospheric ozone (Crutzen, 1970). Nitric oxide (NO), on the other hand, is a highly reactive species that contributes to increasing lower tropospheric ozone concentration (Liu et al., 1999). NO_x also participates in several reactions in which more stable products such as peroxyacetyl-nitrate, nitric acid, and nitrate aerosol are formed. As a result of these reactions, the atmospheric lifetime of NO_x is typically less than 1 d (Derwent et al., 1999).

As a result of its high reactivity, NO is usually converted into more stable products before it has time to be dry deposited. However, dry deposition is important for NO_x and the secondary products such as peroxyacetylnitrate, nitric acid, and the nitrates (Derwent et al., 1999). Wet deposition is equally important for nitrate aerosols. Because of the high reactivity of NO_x , its emissions strongly influence local and regional atmospheric chemistry, while the long lifetime and spectral properties of N_2O result in it having important atmospheric consequences on a global scale (Derwent et al., 1999).

Microbial denitrification and nitrification are the main sources of NO_x and N_2O emitted from soils (Derwent et al., 1999). Chemical denitrification and other kinds of bacterial metabolism involving oxidation or reduction of N also yield trace amounts of the two gases (Smil, 1999). In addition to NO released in the burning of fossil fuels used for various agricultural related activities, NO and NO_x are also formed in the burning of biomass (Andreae, 1991).

Ammonia Loss from Soil

Nelson (1982), in *Nitrogen in Agriculture Soils*, gave an excellent review on gaseous N losses from soil. Rather than reiterating most of this material, we will use this review to mainly provide a research update. Table 8-1 lists some of the characteristics of the studies analyzed. For more detailed information on the principles governing gaseous losses of N from soil, readers are encouraged to examine Nelson's (1982) text.

□ Gaseous Losses other than NH_3

Table 8-1. Characteristics of some of the studies analyzed that used various N sources.

Study†	Year reported	Soil series or description‡	Classification	N sources§	Method	Range of N loss
Al-Kanani et al.	1994	Ste. Rosalie	fine, mixed, nonacid mesic Typic Humaquept	urea	lab incubation 23°C, acid trap (H_3BO_3)	16-21% of urea N applied
Al-Kanani et al.	1991	St. Bernard Ste. Sophie	loamy, mixed, nonacid, frigid Typic Hapludoll; sandy, mixed, nonacid, frigid, Typic Haplorthod	urea, UAN urea, UAN	lab incubation 23-1°C, acid trap (H_3BO_3)	3-55% of urea N applied
Bayraktar and Gezyin	1996	clay loam		urea	field microplots, acid trap (H_3BO_3)	7-24% of urea N analyzed

by fast-growing grass species (Benjamin, 1987). In aquatic ecosystems, nitrification, which may lead to altering et al., 1993).

The volatilization from decomposition of soils, vegetation, oceans, biomass, and animals or emitted from soils and plants of NH_3 exchange has made the exchange measurements to annual net fluxes of NH_3 concentration in ambient NH_3 concentration of NH_3 fluxes to landscape

several ecosystem processes and in the chemistry and physics of the atmosphere. It is chemically active and thus an important source has a lifetime of about 120 yr and is in the stratosphere where it ultimately is destroyed by photolytic reaction catalyzed by a set of atmospheric species that contributes to the depletion of stratospheric ozone (Crutzen, 1970). Nitric oxide is a reactive species that contributes to the depletion of stratospheric ozone. NO_x also produces products such as peroxyacetylnitrates. As a result of these reactions, NO_x has a lifetime of less than 1 d (Derwent et al., 1999). NO_x is usually converted into more stable products such as peroxyacetylnitrates, nitric acid, and nitrate. The deposition of NO_x is equally important as its deposition. The importance of NO_x emissions strongly influences the long lifetime and important atmospheric consequences

are the main sources of NO_x and chemical denitrification and other processes that lead to the reduction of N also yield to the addition to NO released in the atmosphere. NO and NO_2 are related activities (Derwent et al., 1991).

Soil

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Al-Kanani et al.	1991	St. Bernard Site Sophie	loamy, mixed, nonacid, frigid Typic Hapludol; sandy, mixed, nonacid, frigid, Typic Haplorthod	urea, UAN urea, UAN	lab incubation 23°C, acid trap (H_2BO_3)	3–55% of urea N applied
Bayraktir and Gezgir	1996	clay loam		urea	field microplots, acid trap (H_2BO_3)	7–24% of urea N applied
Clay et al.	1990	Esterville (st)	coarse, loamy over sandy, mixed mesic Typic Hapludol	urea	field microplots, acid trap (H_2BO_3)	0–175 mg N $\text{m}^{-2} \text{h}^{-1}$
Fox et al.	1996	Hubersburg (sil)	clayey, illitic mesic, Typic Hapluduit	urea, UAN	field plots, NH_3 sampler micrometeorological	12–35% of applied N
Harme et al.	1997	Chilicotal (vg) Berino (lt)	loamy-skeletal, mixed, thermic, Ustollic Calciorthid; fine, loamy, mixed, thermic Ustollic Haplargid	biosolids	field dynamic NH_3 collectors	8.3–16.6% of applied $\text{NH}_4\text{-N}$
He et al.	1999	Riviera (fs)	loamy, siliceous, hyperthermic, Arenic Glossaqualf	^{15}N labeled AN, U, AS, AS	lab incubation 30°C, sponge trap (H_2PO_4), KCL extraction	16–23% of applied N
Jansen and McGinn	1991	sandy loam		legume green manure	greenhouse pots, acid trap (HCl)	> 1–14% of applied N
Larsson et al.	1998	clay		green mulches	field plots	2–35% of applied N
Lightner et al.	1990	Xenia (sil)	fine-silty, mixed, mesic, Aquic Hapludalf	UUP, AN, urea-KCl, urea- CaCl_2	closed chambers field NH_3 collection, acid trap (H_2SO_4)	12–41% of applied N
Marshall et al.	1998	State (sil) Pacolet (sl) Lily (l)	fine-loamy, mixed, thermic, Typic Hapludults; clayey, kaolinitic, thermic, Typic Hapludults fine-loamy, siliceous, mesic, Typic Hapludults	poultry litter	micrometeorological mass balance	2–6% of applied N

Table cont.

Table 8-1 cont.

Study†	Year reported	Soil series or description‡	Classification	N source§	Method	Range of N loss
Nathan and Mazer	1994	Estherville (sl)	coarse loamy over sandy, mixed, mesic Typic Hapludoll	urea	field microplots, acid trap (H_2BO_3)	1-7% of applied N
Qiyang et al.	1998	Ste. Rosalie (c) Ormstown (scl)	Typic Humaquept Typic Humaquept	turkey manure urea urea-KCl urea-TSP	field microplots, acid trap (H_2SO_4)	1-8% of urea N applied
Ping et al.	2000	loam	Typic Boroll	^{15}N urea	field microplots ^{15}N difference method	avg. 13% of applied N
Quemada et al.	1998	silty clay loam	clayey, carbonatic, calcareous, mesic, Calcixerollic Xerochrept	biosolids (sewage sludge)-DCD	lab incubation 21°C, acid trap (H_2BO_3)	5-71% of applied NH_4^+-N
Schike-Gartley and Sims	1993	Kleij (ls)	siliceous, mesic Aquic Quartzipsamment	poultry litter	lab incubation 23°C, acid trap (H_2BO_3)	4-31% of applied N
Shahandeh et al.	1992	Tifton Dothan	fine, loamy, siliceous, thermic, Plinthic Paleudults, fine loamy, siliceous, thermic Typic Hapludults	nutrasweet sludge urea, AS	lab incubation 25°C, acid trap (H_2PO_3)	>1-19% of applied N
Sommer et al.	1997	loamy sand		pig slurry	field plots, passive flux and acid trap	4-26% of applied NH_4^+-N
Watson and Kipatrick	1991	Hillsbrough (scl), Loughry (scl), Craigavon (c), Portadown (p)		urea (pellet size)	lab incubation 10°C, acid trap	12-17% of applied N
Whitehead and Ralstrick	1990	Balcombe Hucklesbrook, Frlsham, and Andover		MAP, DAP, AS, AN, urea	lab incubation 20°C, acid trap (H_2SO_4)	>1-52% of applied N
Whitehead and Ralstrick	1992	Frlsham (sl)		simulated livestock urine	growth chamber 21°C, acid trap (H_2SO_4)	23-39% of applied N

† Each study is referenced by the first author.

‡ Letters in parentheses indicate soil texture: c, clay; sil, silt loam; vl, very gravelly loam; l, loam; lt, loam taxajunct; fs, fine sand; scl, silty clay loam; ls, loamy sand; sl, sandy loam; scl, sandy clay loam; p, peaty.

§ Capitalized abbreviations indicate N sources: UAN, urea ammonium nitrate; MAP, mono-ammonium phosphate; DAP, diammonium phosphate; AS, ammonium sulfate; AB, ammonia bicarbonates; UUP, urea-urea phosphate; U, urea; DCD, dicyandiamide.

□ Gaseous Losses other than

It is estimated that anthropogenic NH_3 released from livestock production systems is recognized as the major source (1987) estimated that 81% of which accounts for 55% of total NH_3 emissions. It is estimated that livestock accounting for 55% of total NH_3 emissions is dependent on livestock management practices (handling

Land application of organic waste and use of the nutrient in question, the major factor for degradation of surface area on each objective in a given management practice that affects NH_3 loss. Management practices that affect NH_3 loss often utilize management practices that cause increased NH_3 loss reduction. Likewise, emphasis of management practices that reduce NH_3 loss from the organic waste material N

Although most of the N from animal excreta, appreciable N can be emitted into the atmosphere and from decomposing plant material. When fertilizers are applied to soil (Demaree 1994), laboratory conditions commonly be as great as 90% when N is applied. Buffering capacity (Fenn and 1994) are generally less, ranging from 10% to 50%. The reason for greater losses is that conditions are typically set to reduce NH_3 loss while these conditions are in the field environment (Hargrove 1994).

Ammonia volatilization can be grouped into three broad categories: volatilization from unincorporated soils with a pH greater than 7, surface-applied, urea-containing

Items affecting the magnitude of environmental conditions, and management (1994). Factors affecting NH_3 loss from organic waste material include the magnitude of NH_3 volatilization, cation exchange capacity, Ca^{2+} , and urease activity (Hargrove 1994). Environmental factors affecting NH_3 loss are temperature, so (Hargrove 1988). Management

Location (soil)	Year	Urea (pellet size)	Lab incubation 10°C, acid trap	12-17% of applied N
Loughry (scl), Craigavon (c), Portlawn (p)	1990	MAP, DAP, AS, AN, urea	lab incubation 20°C, acid trap (H ₂ SO ₄)	>1-52% of applied N
Batcombe, Hucklebrook, Frisland, and Andover	1992	simulated livestock urine	growth chamber 21°C, acid trap (H ₂ SO ₄)	23-39% of applied N
Frisland (sl)				

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 ‡ Letters in parentheses indicate soil texture: c, clay; sil, silt loam; vgl, very gravelly loam; l, loam; lt, loam taxajunct; fs, fine sand; scl, silty clay loam; ls, loamy sand; sl, sandy loam; scl, sandy clay loam; p, peaty.
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It is estimated that agriculture contributes between 55 and >95% of the anthropogenic NH₃ released annually to the atmosphere (McGinn and Janzen, 1998). Livestock production systems and land application of biosolids are generally recognized as the major sources of atmospheric NH₃. For Europe, Buijsman et al. (1987) estimated that 81% of NH₃ emissions are from livestock while for China, which accounts for 55% of the NH₃ emissions in Asia, Zhao and Wang (1994) estimated that livestock account for 29% of emissions. Total annual emissions are dependent on livestock density, protein intake, animal species, and manure management practices (handling, storage, and land application).

Land application of organic waste materials usually has two objectives, waste disposal and use of the nutrients for plant growth (Rice et al., 1988). When N is the nutrient in question, the major concern for either objective has been the potential for degradation of surface and groundwater. However, the emphasis that is placed on each objective in a given case can be a primary factor in the selection of management practices that affect NH₃ emissions. Emphasis on the waste disposal objective often utilizes management practices that encourage NH₃ volatilization because increased NH₃ loss reduces land requirements and transportation costs for disposal. Likewise, emphasis on the plant nutrient objective will result in the use of management practices that conserve NH₃ and improve plant N use efficiency of the organic waste material N.

Although most of the NH₃ volatilized from the land surface is derived from animal excreta, appreciable amounts may also be derived directly from fertilizers and from decomposing plant material (Whitehead and Raistrick, 1990). Nitrogen can be emitted into the atmosphere as NH₃ when NH₄⁺- or urea-containing fertilizers are applied to soil (Demeyer et al., 1995). The magnitude of NH₃ losses under laboratory conditions commonly ranged from 20 to 60% of the applied N, but can be as great as 90% when N is applied to the surface of sandy soils with very low buffering capacity (Fenn and Hossner, 1985). However, losses under field conditions are generally less, ranging from 0 to 50% of the applied N (Hargrove, 1988). The reason for greater losses in most reported laboratory studies is that laboratory conditions are typically set to create an optimum environment for high rates of NH₃ loss while these conditions seldom exist for sustained periods in a dynamic field environment (Hargrove, 1988).

Ammonia volatilization losses from fertilizer applied to agricultural soils can be grouped into three broad categories: (i) loss from anhydrous NH₃; (ii) NH₃ volatilization from unincorporated, surface-applied, NH₄⁺-containing fertilizer on soils with a pH greater than 7.2; and (iii) NH₃ volatilization from unincorporated, surface-applied, urea-containing fertilizer (Schepers and Fox, 1989).

Items affecting the magnitude of NH₃ loss from soils include soil factors, environmental conditions, and fertilizer management practices (Nathan and Malzer, 1994). Factors affecting NH₃ volatilization losses from fertilizers applied to agricultural soils are typically also important in controlling NH₃ volatilization losses from organic waste material applications. Important soil factors in determining the magnitude of NH₃ volatilization include texture, initial soil pH, pH buffering capacity, cation exchange capacity (CEC), amount of soluble and exchangeable Ca²⁺, and urease activity (Hargrove 1988; Lightner et al., 1990; Nathan and Malzer, 1994). Environmental factors that are important in determining the magnitude of NH₃ loss are temperature, soil water content, and air exchange at the soil surface (Hargrove 1988). Management factors affecting NH₃ loss include time, rate, form,

and method of application, incorporation, time between application and incorporation, depth of application, irrigation, and amount of surface residue (Demeyer et al., 1995; Lightner et al., 1990; Nathan and Malzer, 1994).

Effect of pH on Ammonia Loss

Nitrogen sources with greater potential for raising soil pH after application tend to have greater NH_3 volatilization (He et al., 1999). Ammonia losses increase with higher soil pH because of the increased dissociation of NH_4^+ to NH_3 , thus increasing the potential for volatilization (Sharpe and Harper, 1995). The pH in microsites surrounding urea or NH_4^+ salt granules may be more important in determining NH_3 loss than the overall soil pH (Nelson, 1982; Stumpe et al., 1984).

With urea, NH_3 volatilization only takes place after hydrolysis to ammonium carbonate by the microbially produced enzyme urease. The optimum pH for soil urease activity is between pH 7.0 to 9.0 (Fan and Mackenzie, 1993). The ammonium carbonate resulting from the hydrolysis of urea generates a localized increase in soil pH, which promotes NH_3 volatilization to an extent that is influenced by the initial soil pH and CEC (Whitehead and Raistrick, 1990). Hargrove (1988) concluded that the H^+ buffering capacity of a soil (in this case the resistance to increasing soil pH) is more important than initial soil pH in determining potential NH_3 loss under field conditions. If the soil's buffer capacity is high, the pH rise due to urea hydrolysis will be small and only a small amount of NH_3 will be volatilized. Ferguson et al. (1984) found that the amount of H^+ buffering capacity between a soil's initial pH and a pH of around 7.5 would be more directly related to the expected NH_3 loss than a soil's initial pH when urea is applied.

Buffering capacity can also influence NH_3 volatilization in the opposite way. Normally, H^+ ions resulting from the nitrification process will lower the soil pH and reduce the potential for NH_3 volatilization. If the initial soil pH is sufficiently high for appreciable NH_3 volatilization to occur (>7.5), then the soil's buffering capacity against a decrease in pH influences NH_3 volatilization by allowing it to occur over a longer period of time before the soil's pH is reduced sufficiently to stop NH_3 volatilization (Ferguson et al., 1984; Hargrove, 1988). As such, the buffering capacity against an increase in pH (from urea hydrolysis) is most important in noncalcareous soils, while the buffering capacity against a decrease in pH (mainly from nitrification) is most important in calcareous soils (Hargrove, 1988).

Effect of Cation Exchange Capacity on Ammonia Loss

Although H^+ buffering capacity and CEC are related, soil CEC is also important for NH_3 volatilization because it provides a mechanism by which NH_4^+ ions are removed from soil solution, thereby reducing the total amount of ammoniacal N in the soil solution at any given time that is subject to volatilization (Hargrove, 1988). The influence of CEC is less than that of H^+ buffering capacity in terms of magnitude of NH_3 loss (Rachhpal-Singh and Nye, 1986).

Effect of Soil Texture and Organic Matter on Ammonia Loss

A number of investigators have noted that increased organic matter (OM) and clay content of soil reduced NH_3 loss (Al-Kanani et al., 1991; Hargrove, 1988; Whitehead and Raistrick, 1990). The reduction in NH_3 loss is usually ascribed to

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between application and incorporation of surface residue (Demeyer et al., 1994).

Ammonia Loss

Raising soil pH after application (Hargrove, 1999). Ammonia losses increase dissociation of NH_4^+ to NH_3 , thus urea and Harper, 1995). The pH increases may be more important in desert soils (Hargrove, 1982; Stumpe et al., 1984).

Urea after hydrolysis to ammonium increases urease. The optimum pH for soil urease is 7.5 (Mackenzie, 1993). The ammonium urea generates a localized increase in pH to an extent that is influenced by soil texture (Hargrove, 1990). Hargrove (1988) concludes that in this case the resistance to increasing pH in determining potential NH_3 volatilization is high, the pH rise due to amount of NH_3 will be volatilized. H^+ buffering capacity between a pH of 6.5 and 7.5 is more directly related to the extent of urea applied.

Volatilization in the opposite way. A process will lower the soil pH if the initial soil pH is sufficiently high (>7.5), then the soil's buffering capacity will allow it to reduce its pH sufficiently to allow volatilization (Hargrove, 1988). As such, the buffer capacity of hydrolysis is most important in soils against a decrease in pH (mainly in desert soils (Hargrove, 1988).

Soil CEC on Ammonia Loss

Related, soil CEC is also important mechanism by which NH_4^+ ions are held. The total amount of ammoniacal N subject to volatilization (Hargrove, 1988). Buffering capacity in terms of pH (Hargrove, 1986).

Organic Matter on Ammonia Loss

Increased organic matter (OM) (Al-Kanani et al., 1991; Hargrove, 1988; Hargrove, 1988). NH_3 loss is usually ascribed to

the relative contribution of the OM and clay components to the CEC of the soil (Al-Kanani et al., 1991; O'Toole et al., 1985). Al-Kanani et al. (1991) also observed that the effect of clay content on NH_3 volatilization became more pronounced as soil approached air dryness.

Effect of Urease Activity on Ammonia Loss

Almost all agricultural soils are considered to have adequate concentrations of urease for fairly rapid hydrolysis of urea (Hargrove, 1988). However, at higher urease activity, applied urea will be hydrolyzed more rapidly before it can move deeper into the soil (Rachhpal-Singh and Nye, 1986). This will result in higher NH_3 loss potentials because of the increase in ammoniacal N concentrations at the soil surface along with the associated rise in surface soil pH from urea hydrolysis. Vegetation and crop residue are known to increase urease activity (Schilke-Gartley and Sims, 1993). McInnes et al. (1986) reported that urease activity on wheat (*Triticum aestivum* L.) straw was 20 times that of the soil just below it. Also, the length of time since the soils last received urine or urea may have an effect on initial urease activity (Whitehead and Raistrick, 1990).

Effect of Temperature on Ammonia Loss

He et al. (1999) found that potential maximum NH_3 volatilization increased twofold when the temperature increased from 5 to 25°C, and threefold when temperature increased from 25 to 45°C. They concluded the greatly enhanced NH_3 volatilization at 45°C compared with 25°C was related to the inhibition of nitrification at the high temperature, which increased the availability of ammoniacal N for NH_3 volatilization over a prolonged period of time. Hargrove (1988) reported temperature influences the magnitude of NH_3 loss in several ways:

- It increases urease activity, thereby increasing urea hydrolysis rate. A faster hydrolysis rate results in higher soil pH and greater NH_4^+ concentrations near the soil surface.
- It influences the $\text{NH}_4^+/\text{NH}_3$ equilibrium and the equilibrium between NH_3 in solution and NH_3 gas, resulting in a higher proportion of ammoniacal N being present as NH_3 gas.
- It influences the diffusion of urea- and ammoniacal N and bicarbonate ions.
- It increases the solubility of CaCO_3 and of Ca reaction products in calcareous soils.

Effect of Soil Water Content on Ammonia Loss

The influence of soil water content on NH_3 volatilization is generally straightforward for laboratory studies. If the hydrolysis of urea is not inhibited by the low moisture content, a lower moisture content means a higher NH_3 concentration and a higher pH effect resulting in the largest total NH_3 losses and highest average NH_3 volatilization rates (Demeyer et al., 1995). On the other hand, the influence of soil water content on NH_3 volatilization under dynamic field conditions is very complex and has been difficult for scientists to determine, especially where soil water content fluctuates widely on a daily basis due to the combined effects of upward movement of water in the soil, dew formation, and evaporation (Hargrove, 1988). Bouwmeester et al. (1985) observed that highest total NH_3 losses occurred

when wet soil conditions were maintained by air humidities between 80 and 95% with essentially no rainfall. The diurnal pattern of NH_3 volatilization loss, with maximum loss near midday, is associated with temperature increases and dew water evaporation that results in increases in NH_4^+ -N concentration in the aqueous phase and in the partial pressure gradient of NH_3 leading to enhanced NH_3 volatilization (Lightner et al., 1990; Nathan and Malzer, 1994).

Hargrove (1988) listed several relationships that have emerged from field studies:

- For maximum NH_3 losses, the soil water content must be at or near field capacity at the time of fertilizer application. If the soil is dry, dissolution of dry fertilizer materials is slow and the biological and chemical reactions necessary for volatilization are very slow or do not occur at all.
- On a daily basis, maximum NH_3 loss rates occur when the soil surface is drying. As the soil dries, the concentration of NH_3 in the soil solution increases resulting in NH_3 being lost to the atmosphere to maintain equilibrium with NH_4^+ . Slow drying of a wet soil results in more NH_3 loss than rapid drying.
- If the soil surface dries but is not rewetted by dew or light rainfall, NH_3 loss is reduced because of insufficient moisture for the necessary biochemical and chemical reactions.
- If rainfall is sufficient to move the N source into the soil profile, NH_3 volatilization ceases.

Effect of Wind Speed on Ammonia Loss

If a steady supply of NH_3 is available, increasing wind speed would promote more rapid transport of NH_3 away from the soil surface by maintaining a lower partial pressure of NH_3 over the soil surface (Sharpe and Harper, 1995). However, wind generally has a drying effect on soil that in turn can influence opposite outcomes. Nathan and Malzer (1994) concluded that the drying effect caused by higher wind speeds would result in higher solution concentrations of NH_3 at the soil surface, resulting in higher NH_3 volatilization. Bouwmeester et al. (1985) noted that wind can impede the volatilization of NH_3 by rapidly drying the topsoil and reducing the rate at which underlying urea moves to the soil surface, thus acting as a physical barrier. They further stated that their results indicated that when the relative humidity of the air is high, soil moisture content may remain high enough to promote NH_3 losses.

Effect of Management Practices on Ammonia Loss

Hargrove (1988) concluded that soil properties largely determine the potential for loss, but environmental conditions determine the actual magnitude of loss under field conditions. Management factors influence the magnitude of loss by modifying the soil properties and/or environmental conditions. As mentioned above, some of the management factors affecting NH_3 loss include time, rate, form, and method of application, incorporation, time between application and incorporation, depth of application, irrigation, and amount of surface residue.

Generally, NH_3 losses increase with increasing amounts of urea or NH_4^+ added to the soil. Studies have shown that these losses may be linear or exponential such that the relative loss (as percentage of the applied N) may decrease, remain constant, or increase with increasing application rates (Hargrove, 1988). In addition,

Gaseous Losses other than through

tion, the NH_3 loss potential for urea-ammonium nitrate (UAN) soils, but greatest with (i) calcareous soils.

A number of chemical or physical methods to reduce NH_3 volatilization losses include: (i) coating urea to that retard hydrolysis of urea by physical and/or chemical characteristics; (ii) addition of acidifying agents to urea to form insoluble salts of Ca, Mg, and/or carbonates and thereby reduce losses (Buresh and Baanante, 1993; A). These methods have been successful in the development of additives that are effective in improving the efficiency of urea.

Maximum NH_3 losses occur when urea is broadcast on the soil surface. Band application and incorporation reduce NH_3 losses. Significant reduction in losses may be expected because bands are exposed to fewer environmental conditions than broadcast applications. It has been reported for fertilizer granules that incorporation of animal waste slurries reduces losses (Sommer et al., 1997). One study has shown that slurries promote infiltration.

Direct injection or incorporation reduces NH_3 loss (Hargrove, 1988). Bouwmeester et al. (1985) found that if 2.5 cm of water was applied before injecting urea at a depth of 2.5 cm. Significant losses from injected anhydrous ammonia were reduced to a depth of at least 5 cm. The depth to which injected urea moves is dependent on soil characteristics; such as texture, moisture, and temperature. In sandy soils, the depth is from 5 to 10 cm (Hargrove, 1988). The factor in NH_3 volatilization when injecting with anhydrous ammonia, 50% of the NH_3 can be lost when the large portion of the injected N moves upward movement of the water. This reduces NH_3 losses. It has also been demonstrated that slurry injected directly into a cell reduces losses for the same reasons (Sommer and Erwin, 1990).

Ammonia volatilization is affected by soil moisture. However, it is not the soil moisture that affects NH_3 volatilization. Clay and organic matter affect maximum soil temperature

in humidities between 80 and 95% of NH_3 volatilization loss, with temperature increases and dew point NH_4^+ -N concentration in the aqueous solution of NH_3 leading to enhanced NH_3 loss (Malzer, 1994).

Factors that have emerged from field

studies must be at or near field capacity. If the soil is dry, dissolution of dry fertilizer and chemical reactions necessary for NH_3 volatilization do not occur at all.

NH_3 volatilization occurs when the soil surface is dry. As NH_4^+ in the soil solution increases, there is a tendency to maintain equilibrium with the atmosphere, resulting in more NH_3 loss than rapid drying.

Following dew or light rainfall, NH_3 loss is reduced for the necessary biochemical

processes into the soil profile, NH_3 volatilization is reduced.

Ammonia Loss

Increasing wind speed would promote NH_3 loss from the soil surface by maintaining a lower relative humidity (Hargrove and Harper, 1995). However, wind can influence opposite outcomes: the drying effect caused by high concentrations of NH_3 at the soil surface (Bouwmeester et al., 1985) noted by rapidly drying the topsoil and exposing it to the soil surface, thus acting as a barrier to NH_3 loss. Results indicated that when the soil moisture content may remain high enough

Factors on Ammonia Loss

Factors largely determine the potential magnitude of loss under actual conditions. As mentioned, NH_3 loss include time, rate, form, and location of application and incorporation of surface residue.

Amounts of urea or NH_4^+ added may be linear or exponential (Applied N) may decrease, remain constant (Hargrove, 1988). In addition,

the NH_3 loss potential for fertilizers is greatest with urea, intermediate with urea-ammonium nitrate (UAN) solution, and least with NH_4^+ salts on noncalcareous soils, but greatest with $(\text{NH}_4)_2\text{SO}_4$ and much less with urea or NH_4NO_3 on calcareous soils.

A number of chemical or fertilizer modification methods have been used to reduce NH_3 volatilization losses from urea applications. The most studied methods include: (i) coating urea to slow its rate of dissolution; (ii) use of compounds that retard hydrolysis of urea by reducing the activity of urease; (iii) changing the physical and/or chemical characteristics of the soil microenvironment with the addition of acidifying agents to decrease NH_3 volatilization loss; and (iv) mixing soluble salts of Ca, Mg, and/or K with urea to promote the formation of insoluble carbonates and thereby reduce the rise in pH and concentration of NH_3 in the soil (Buresh and Baanante, 1993; Al-Kanani et al., 1994; Bayrakli and Gezgin, 1996). These methods have been successful to varying degrees and work continues on the development of additives that are economically feasible, environmentally safe, and effective in improving the efficiency of urea fertilizer.

Maximum NH_3 losses occur when N fertilizers and organic waste materials are broadcast on the soil surface (Hargrove, 1988; Nathan and Malzer, 1994). Surface band application and incorporation/injection are often employed to minimize NH_3 losses. Significant reduction in NH_3 losses from surface band applications (including increasing fertilizer granule size) compared with broadcast applications may be expected because banded applications will be in contact with less soil and exposed to fewer environmental factors. Contradictory effects or no effect have been reported for fertilizer granule size with surface applications of urea on NH_3 loss (Black et al., 1987; Watson and Kilpatrick 1991). However, surface band application of animal waste slurries has shown significant reduction in NH_3 volatilization (Sommer et al., 1997). One reason they gave for this is that surface banding of slurries promotes infiltration.

Direct injection or incorporation of N fertilizers results in much reduced or no NH_3 loss (Hargrove, 1988). Bouwmeester et al. (1985) found no NH_3 volatilization if 2.5 cm of water was applied immediately after urea application or when banding urea at a depth of 2.5 cm. Schepers and Fox (1989) conclude that volatilization losses from injected anhydrous NH_3 can be assumed to be minimal if the NH_3 is injected to a depth of at least 5 cm and if the furrow behind the injector seals completely. The depth to which incorporation or injection is necessary depends on the soil characteristics; such as texture, density, CEC, OM content, etc., but for most soils is from 5 to 10 cm (Hargrove, 1988). Soil moisture content is also an important factor in NH_3 volatilization when direct injecting N supplying materials. Working with anhydrous ammonia, Sommer and Christensen (1992) found that up to 50% of the NH_3 can be lost when injected into a wet soil. They concluded that a large portion of the injected NH_3 is retained by absorption in the soil water and upward movement of the water due to evaporation may be the cause of the large NH_3 losses. It has also been demonstrated that NH_3 loss may be high from animal slurry injected directly into a compressed and excessively wet soil for some of the same reasons (Sommer and Ersboll, 1994).

Ammonia volatilization is also affected by the amount of crop residue present on the soil surface. However, there are conflicting reports on how crop residues affect NH_3 volatilization. Clay et al. (1990) reported that residue cover reduced the daily maximum soil temperature and increased the soil water content resulting in

reduced NH_3 volatilization losses. Schilke-Gartley and Sims (1993) found either no effect or reduced losses when animal manure was applied to corn (*Zea mays* L.) and soybean [*Glycine max* (L.) Merr.] residues in the spring of the year. They suggest one possible reason for their results is reduced urease activity in the residues resulting from environmental exposure over the fall and winter months. In contrast, Hargrove (1988) drawing from numerous studies, states that crop residues generally increase NH_3 losses in several ways:

- By its associated higher urease activity compared with soil;
- By promoting slow drying of the soil surface, thereby maintaining higher loss rates for a longer period of time; and
- By forming a physical barrier between the N source and the soil.

In addition, Whitehead and Raistrick (1990) concluded that leaf litter allows increased NH_3 volatilization by increasing the surface area for urease activity and volatilization to occur. Fenn and Hossner (1985) suggest that higher urease activity may apply only to growing crops and fresh residues rather than older residues that may have been exposed to sunlight, high temperatures, and drying conditions that can result in urease degradation.

Living plants can also be great modifiers and significantly influence volatile NH_3 loss from soils. Actively growing plants influence both the soil's temperature and water regimes and also can have strong effects on the soil-air boundary layer. The plant's ability to both absorb and release atmospheric NH_3 must be taken into account. Foliar absorption of NH_3 contributed significantly to the reduction in NH_3 loss when animal wastes were applied in the spring to a dense and actively growing plant cover (Marshall et al., 1998; Sommer et al., 1997). Effect of growing plants on NH_3 loss will be discussed in more detail in the following section.

Our inability to accurately predict environmental factors such as soil temperature, soil water content (especially the thin surface layer), soil water flux, and wind speed on the field or ecosystem level will always limit our ability to accurately predict NH_3 volatilization under field conditions.

Ammonia Loss from Plants

Farquhar et al. (1980) were one of the first to report on the existence of an NH_3 compensation point for plants. The compensation point for NH_3 is defined as the molar fraction at which the net exchange between plants and the atmosphere is zero. The existence of an NH_3 compensation point implies that vegetation has a major influence on the transport and budgets of atmospheric NH_3 (Nielsen and Schjoerring, 1998). The NH_3 compensation point allows plants to act as both sink and source for atmospheric NH_3 . At ambient NH_3 concentrations above the compensation point, NH_3 is absorbed by leaves, while at concentrations below the compensation point NH_3 is lost to the atmosphere.

Ammonium is the only inorganic N compound that can be used directly as a precursor for the biosynthesis of organic N products in plants (Lea, 1997). As a consequence, substantial concentrations of NH_4^+ may exist in the leaf and in the apoplastic solution. The concentration of NH_4^+ and H^+ in the leaf apoplastic solution determines the size of the NH_3 compensation point (Husted and Schjoerring, 1996). It is generally accepted that free NH_3 can diffuse across leaf cell membranes

□ Gaseous Losses other than

without the involvement of nium is constantly generated as photorespiration, nitrate (Leegood et al., 1995). For NH_4^+ released during these cated directly to the leaves fr

The major pathway of N the glutamine synthetase/glu chloroplast (Schjoerring et al., a transporter with channel-like idly to changes in apoplastic l with mutants of barley (*Horde significance of GS in controlling Schjoerring et al. (2000) also re stantial increase in apoplastic f high NH_3 compensation point tus, rapid absorption of NH_4^+ f NH_4^+ is constantly generated ir ties are critical in controlling N*

Factors Influenc

The NH_3 compensation p of physiological and environm nitude and direction of the N scales, depending on environ timing of fertilizer application of the major factors influencing

Nitrogen Status and pH

Theoretically, the NH_3 con be determined by knowing the face (apoplast). Husted and Sc trations for oilseed rape plant: with plant N status while apop independent of plant N status. difference in apoplastic pH of H^+ concentrations in the apopla for most plants, a lower pH in will still play an important rol Even under conditions in whic times lower than the extracellu 7.5) and in the chloroplasts (ap plastic solution (approximate directed toward the apoplast (

The loss of NH_3 from the tus of the canopy for wheat (N 1993), oilseed rape (Husted an The concentration of NH_4^+ in t

and Sims (1993) found either as applied to corn (*Zea mays* L.) in the spring of the year. They suggest urease activity in the residues in fall and winter months. In conclusion, states that crop residues

pared with soil;

ce, thereby maintaining higher

source and the soil.

concluded that leaf litter allows surface area for urease activity and suggest that higher urease activities in newer rather than older residues at higher temperatures, and drying conditions

significantly influence volatile emissions both the soil's temperature and moisture on the soil-air boundary layer. Atmospheric NH_3 must be taken into account significantly to the reduction of emissions in the spring to a dense and actively growing crop (Lambert et al., 1997). Effect of growing conditions is discussed in the following section.

Environmental factors such as soil temperature, soil water flux, and soil moisture limit our ability to accurately estimate emissions.

Plants

Report on the existence of an NH_3 compensation point for NH_3 is defined as the point at which plants and the atmosphere are in equilibrium. It implies that vegetation has a net sink for atmospheric NH_3 (Nielsen and Schjoerring, 1998). It allows plants to act as both sink and source of NH_3 at concentrations above the compensation point and at concentrations below the compensation point.

It is noted that can be used directly as a sink for NH_3 in plants (Lea, 1997). As a result, NH_3 may exist in the leaf and in the soil. The H^+ in the leaf apoplastic solution is a key factor in the NH_3 compensation point (Husted and Schjoerring, 1996). The use across leaf cell membranes

without the involvement of a membrane translocator (Baron et al., 1994). Ammonium is constantly generated in large quantities in plant leaves by processes such as photorespiration, nitrate reduction, protein turnover, and lignin biosynthesis (Leegood et al., 1995). For plants to efficiently utilize N they must be able to recycle NH_4^+ released during these catabolic reactions. In addition, NH_4^+ may be translocated directly to the leaves from the roots (Cramer and Lewis, 1993).

The major pathway of NH_4^+ assimilation and reassimilation in plant leaves is the glutamine synthetase/glutamate synthase (GS/GOGAT) cycle occurring in the chloroplast (Schjoerring et al., 1998). Ammonium is retrieved by a system involving a transporter with channel-like properties that seem to be able to respond very rapidly to changes in apoplastic NH_4^+ concentration (Schjoerring et al., 2000). Working with mutants of barley (*Hordeum vulgare* L.), Mattsson et al. (1998) demonstrated the significance of GS in controlling the flux of NH_3 between plants and the atmosphere. Schjoerring et al. (2000) also reported that inhibition of GS leads to a rapid and substantial increase in apoplastic NH_4^+ concentration. Schjoerring et al. (1998) noted that high NH_3 compensation points seemed to always be the result of high tissue N status, rapid absorption of NH_4^+ from the root medium and/or low activity of GS. Since NH_4^+ is constantly generated in large amounts in leaf tissues, GS and GOGAT activities are critical in controlling NH_3 emission from plant leaves.

Factors Influencing Ammonia Losses from Plants

The NH_3 compensation point is a variable parameter influenced by a range of physiological and environmental conditions (Schjoerring et al., 1998). The magnitude and direction of the NH_3 fluxes may change on hourly, daily, and seasonal scales, depending on environmental conditions, crop growth characteristics, and timing of fertilizer application (Sutton et al., 1994). Only a brief discussion of some of the major factors influencing NH_3 losses from plants will be covered.

Nitrogen Status and pH

Theoretically, the NH_3 compensation point at any given leaf temperature can be determined by knowing the concentration of NH_4^+ and H^+ in the aqueous interface (apoplast). Husted and Schjoerring (1996) reported apoplastic NH_4^+ concentrations for oilseed rape plants (*Brassica napus* L.) increased at all growth stages with plant N status while apoplastic pH values remained fairly constant and were independent of plant N status and plant ontogeny. Dannel et al. (1995) found little difference in apoplastic pH of plants grown with NO_3^- or NH_4^+ as the N source. If H^+ concentrations in the apoplastic solution remain fairly constant during growth for most plants, a lower pH in the apoplast than in surrounding leaf components will still play an important role in the diffusion of dissolved NH_3 within leaves. Even under conditions in which the intracellular NH_4^+ concentration is 10 to 100 times lower than the extracellular concentration, a high pH in the cytoplasm (7.0–7.5) and in the chloroplasts (approximately 8.0 in light) relative to that in the apoplastic solution (approximately 6.0) may maintain a gradient of dissolved NH_3 directed toward the apoplast (Nielsen and Schjoerring, 1998).

The loss of NH_3 from the canopy has been found to increase with the N status of the canopy for wheat (Morgan and Parton, 1989), barley (Schjoerring et al., 1993), oilseed rape (Husted and Schjoerring, 1996), and corn (Francis et al., 1993). The concentration of NH_4^+ in the leaf apoplastic solution is very sensitive to leaf

N status and external N supply (Nielsen and Schjoerring, 1998). Husted and Schjoerring (1996) reported that increasing plant N status resulted in increased bulk tissue NH_4^+ concentration and also increased apoplastic NH_4^+ concentration at all growth states. Mattsson and Schjoerring (1996) found that plants having access to NH_4^+ in the root medium had higher apoplastic NH_4^+ concentrations than plants absorbing NO_3^- , and that leaf apoplastic NH_4^+ concentration increases with NH_4^+ concentration in the root medium.

Growth Stage

Bulk tissue NH_4^+ concentrations change with plant ontogeny. Morgan and Parton (1989) attribute increased potential for NH_3 volatilization during later developmental stages to genetic changes in plant metabolism that elevated tissue NH_4^+ concentrations above those occurring in younger, vegetative tissue. They related periods of increased NH_3 volatilization from anthesis through maturity to changes in the balance between NH_4^+ -releasing reactions (deamination, senescence-induced proteolysis, and nitrate reduction) and NH_4^+ uptake reactions (N transport and NH_4^+ assimilation). As the balance shifts in favor of NH_4^+ -releasing reactions, there is the establishment of new, higher, steady-state tissue NH_4^+ concentrations. Schjoerring et al. (1998) also reported that the NH_3 compensation point depends on plant developmental stage with peaks in NH_3 emission related to leaf senescence and N remobilization.

Temperature

The high sensitivity of plant-atmosphere NH_3 exchange to leaf temperature makes information about temperature very important when data on NH_3 compensation points are reported (Husted and Schjoerring, 1996). In one of the earliest studies on temperature effects on volatile N loss from plants, Stutte and da Silva (1981) found that increasing air temperature from 30 to 35°C greatly increased the rate of volatile N loss for all eight rice (*Oryza sativa* L.) cultivars tested. Based on their results, they postulated volatile N losses occurred in conjunction with transpirational water vapors and may constitute a defense mechanism of plants against NH_3 toxicity under temperature stress. Schjoerring et al. (1998) also noted that simply increasing the temperature from 15 to 30°C can cause plants to switch from being strong sinks for atmospheric NH_3 to being significant NH_3 sources. Husted and Schjoerring (1996) reported increasing leaf temperatures from 10 to 35°C caused an exponential increase in NH_3 emission from plants exposed to low ambient NH_3 concentrations, indicating that leaf conductance was not the only factor responding to the temperature increase. They noted when simple thermodynamics equations were used in combination with NH_3 compensation points derived from measurements of apoplastic NH_4^+ concentrations, increased NH_3 emissions with increasing temperature could be explained in their study entirely in terms of effects on the equilibrium between gas phase and soluble NH_3 and NH_4^+ in the apoplast. The profound influence of temperature on plant-atmosphere NH_3 exchange is partly via affecting the concentration of atmospheric NH_3 in equilibrium with NH_3 in the apoplastic solution, and partly via affecting the physiological processes generating or assimilating NH_4^+ in the leaf tissues (Schjoerring et al., 1998).

□ Gaseous Losses other than th

Wind, Humidity, and Light

In addition to temperature, light intensity can influence plant delivery to or removal of NH_3 from between leaves and air will present such a layer will slow down NH_3 losses (Holtan-Hartwig and Schjoerring, 1996) observed that at low relative humidity at low light intensity of a humidities, NH_3 uptake did not occur. Stomata in a dry atmosphere compared with a humid atmosphere are favored by high light intensities (Husted and Schjoerring, 1996). A control mechanism for the regulation of stomatal conductance for NH_3 diffusion.

It is generally reported that maximum NH_3 emission near midday and Bockman, 1994). Strong diurnal trends in NH_3 exchange in studies investigating C_3 plants. free NH_3 that must pass out of the GAT pathway (Leegood et al., 1992) is very large with rates up to 10 $\mu\text{mol m}^{-2} \text{s}^{-1}$ (Joy et al., 1992). Holtan-Hartwig (1992) probably is the effect of light on stomatal conductance. The diurnal trend in NH_3 exchange is similar to diurnal variations in NH_3 exchange temperature along with stomatal conductance. The exchange of NH_4^+ and H^+ in the leaf is absent in C_4 plants and the major sink for NH_3 in C_4 plants is generally much less than in C_3 plants. The difference between C_3 and C_4 plants would suggest that temperature and concentration (Leegood et al., 1992) diurnal trends in NH_3 emission.

Atmospheric Ammonia Concentration

Ambient NH_3 concentration affects the NH_3 compensation point in the absence of other factors (Leegood et al., 1992). Increased livestock production has led to increased NH_3 emissions from agricultural sources and atmospheric NH_3 concentrations have increased in leaves and ambient air. ApSimor (1992) estimated emissions over Europe between 1950 and 1990. This would serve as net sinks for atmospheric NH_3 and ice core data from central Green

Schjoerring, 1998). Husted and Schjoerring (1996) reported that plants having access to NH_4^+ concentrations higher than plants without access to NH_4^+ have higher NH_4^+ concentrations in the apoplast. This concentration increases with NH_4^+ concentration.

With plant ontogeny, Morgan and Schjoerring (1996) reported that NH_3 volatilization during later development was higher in older, vegetative tissue than in younger, vegetative tissue. They found that from anthesis through maturity, NH_3 exchange reactions (deamination, senescence) and NH_4^+ uptake reactions (N assimilation) shifted in favor of NH_4^+ release. Higher, steady-state tissue NH_4^+ concentrations supported that the NH_3 compensation point peaks in NH_3 emission related to NH_4^+ concentration.

NH_3 exchange to leaf temperature is important when data on NH_3 compensation point are used (Schjoerring, 1996). In one of the earliest studies, Stutte and da Silva (1981) found that at 35°C greatly increased the rate of NH_3 exchange in cultivars tested. Based on their results in conjunction with transpirational characteristics of plants against NH_3 toxicity (Schjoerring, 1998) also noted that simply increasing ambient NH_3 concentrations to switch from being strong sinks to sources. Husted and Schjoerring (1996) found that 10 to 35°C caused an exponential increase in ambient NH_3 concentrations, a factor responding to the temperature dynamics equations were used in conjunction with measurements of apoplastic NH_3 concentrations with increasing temperature. The effects of effects on the equilibrium between apoplast and atmosphere. The profound influence of temperature is partly via affecting the concentration of NH_3 in the apoplastic solution, thus generating or assimilating NH_4^+ .

Wind, Humidity, and Light Intensity

In addition to temperature, various parameters such as wind, humidity, and light intensity can influence plant-atmosphere NH_3 fluxes. Wind will affect the delivery to or removal of NH_3 from the exchange surface. A stagnant boundary layer between leaves and air will prevent NH_3 diffusion, and circumstances that preserve such a layer will slow down the exchange rate while gusty winds may enhance NH_3 losses (Holtan-Hartwig and Bockman, 1994). Studying the combined effects of variations in light intensity and air humidity on NH_3 fluxes, Husted and Schjoerring (1996) observed that at low relative humidity (20%) NH_3 absorption reached a maximum at low light intensity of approximately $350 \mu\text{mol m}^{-2} \text{s}^{-1}$, whereas at higher air humidities, NH_3 uptake did not saturate below $600 \mu\text{mol m}^{-2} \text{s}^{-1}$. This reflects that stomata in a dry atmosphere reached full aperture at low light intensity as compared with a humid atmosphere. Under humid conditions NH_3 exchange would be favored by high light intensities, whereas relatively large NH_3 exchange rates may be found under dry atmospheric conditions, even when light intensities are low (Husted and Schjoerring, 1996). Thus, change in stomatal opening is an important control mechanism for the regulation of NH_3 flux into or out of leaves because of its effect on conductance for NH_3 diffusion (Schjoerring et al., 1998).

It is generally reported that NH_3 emission follows a diurnal trend with maximum emission near midday and minimum emission at night (Holtan-Hartwig and Bockman, 1994). Strong diurnal trend reports are typically associated with studies investigating C_3 plants. Each photorespiration cycle in C_3 plants yields a free NH_3 that must pass out of the mitochondria for reassimilation by the GS/GO-GAT pathway (Leegood et al., 1995). The rate of NH_3 release by photorespiration is very large with rates up to 10 times that generated by the reduction of nitrate (Joy et al., 1992). Holtan-Hartwig and Bockman (1994) summarized that it probably is the effect of light on stomata opening and on photorespiration that produce the diurnal trend in NH_3 exchange. However, Schjoerring et al. (2000) report that diurnal variations in NH_3 exchange seem to be caused mainly by changes in leaf temperature along with stomatal conductance rather than changes in concentrations of NH_4^+ and H^+ in the leaf apoplastic solution. Photorespiration is essentially absent in C_4 plants and the magnitude for diurnal trends in NH_3 emission from C_4 plants is generally much less than for C_3 plants. Comparing NH_3 emissions between C_3 and C_4 plants would suggest that stomatal conductance along with both temperature and concentration (NH_3 release activities) combine to cause the larger diurnal trends in NH_3 emission from C_3 vs. C_4 plants.

Atmospheric Ammonia Concentration

Ambient NH_3 concentrations near the canopy should approach the NH_3 compensation point in the absence of other sources or sinks (Langford and Fehsenfeld, 1992). Increased livestock production and N fertilizer use since 1950 would suggest increased NH_3 emissions from agricultural activities that would produce increased atmospheric NH_3 concentrations resulting in lower concentration gradients between leaves and ambient air. ApSimon et al. (1987) reported a 50% increase in NH_3 emissions over Europe between 1950 and 1980 mainly as the consequence of intensive agricultural practices. This would suggest an increased potential for vegetation to serve as net sinks for atmospheric NH_3 over the last 50 yr. However, in studying ice core data from central Greenland, Laj et al. (1992) concluded that atmospheric

NH_3 concentrations have actually decreased over the last 50 yr. Their explanation for decreasing atmospheric NH_3 concentrations is the rapid reactions between atmospheric NH_3 and acidic aerosols of S and N which themselves have increased in concentrations by three- to fourfold over the last 250 yr. Reactions decreasing atmospheric NH_3 concentrations would enhance NH_3 losses from crop canopies.

Concentrations of NH_3 -N in air in rural areas is generally within the range from 1 to $14 \mu\text{g m}^{-3}$, with about 1 to $6 \mu\text{g m}^{-3}$ as typical (Holtan-Hartwig and Bockman, 1994). Farquhar et al. (1980) found the NH_3 compensation point for young plants of several species to be about 1 to $4 \mu\text{g NH}_3\text{-N m}^{-3}$. When the NH_3 compensation point fluctuates about the atmospheric NH_3 concentration, NH_3 may be either absorbed or emitted by these young plants. Morgan and Parton (1989) reported that the compensation point for wheat increases as plants approach maturity, from about $13 \mu\text{g NH}_3\text{-N m}^{-3}$ at early grain filling, to $23 \mu\text{g NH}_3\text{-N m}^{-3}$ at late grain filling. Mattsson et al. (1998) showed approximately a 10-fold increase in NH_3 compensation point, 2.5 to $26 \mu\text{g NH}_3\text{-N m}^{-3}$, for oilseed rape when going from low to high external N supply. The NH_3 concentration gradient between the atmosphere and the leaf apoplastic solution stands as the major driving force for NH_3 gains and losses in plants.

Carbon Substrates and Plant Stress

Assimilation of NH_4^+ depends on an adequate supply of C in the form of 2-oxoglutarate, an intermediate of the mitochondrial tricarboxylic acid cycle (Schjoerring et al., 2000). The availability of C substrates may also determine how efficiently NH_3 is reassimilated in plants. Remobilization of N during the reproductive growth phase combined with nonoptimal photosynthetic conditions (e.g., drought, disease, etc.) may give an excess of N relative to C and result in NH_3 losses (Holtan-Hartwig and Bockman, 1994). Papakosta and Gagianas (1991) noted that N losses were related to both N content at anthesis and grain yield for winter wheat (*Triticum* spp.). Schjoerring et al. (1993) reported similar findings that NH_3 losses are related to N harvest index (ratio between grain N content and total shoot N content). High N harvest indices are achieved when favorable climatic conditions produce high grain yields (high C substrates) and effective deposition in the grain of N mobilized from vegetative plant parts. Therefore, NH_3 emission will change with year-to-year variations in weather that control C substrate production and crop N economy (Schjoerring et al., 1993).

Emissions from Live Agricultural Plants

Methods used for measuring NH_3 exchange between air and crops can be grouped in three main categories and all have problems estimating annual NH_3 emissions from plants. Enclosure or chamber methods have difficulty matching natural factors that have important influences on the volatilization of NH_3 over the full growth cycle, such as evaporation rate, temperature, wind speed, ambient NH_3 concentration and dew formation (Holtan-Hartwig and Bockman, 1994). Conventional micrometeorological methods typically have problems with temporal and spatial variability, short time scales, and the requirement for uniform, level surface sources with long fetches and one-dimensional vertical flux densities (Holtan-Hartwig and Bockman, 1994). Conventional micrometeorological techniques also do not strictly measure NH_3 losses from plants, but give a combined

□ Gaseous Losses other than

NH_3 flux from plants and quantity of aboveground plant material can be masked by condensation. Condensation also cannot differentiate if NH_3 is used with standing N methanogenesis and substitution occur. This is a problematic error in estimation (Schjoerring et al., 1997; Harper and Sharpe, 1997).

The bidirectional nature of NH_3 exchange and the large spatial variability of NH_3 fluxes make the extrapolation of current data to landscape scale a speculative exercise. A comprehensive list of NH_3 losses found in different plant species and development stages from reported studies are from Cerre et al. (1994) and Bockman, (1994) found $1.5 \text{ kg NH}_3\text{-N ha}^{-1} \text{ d}^{-1}$, but conclude that yearly losses as emissions from crops and plant development stage are not a good estimate for net NH_3 losses from crops, $1.5 \text{ kg NH}_3\text{-N ha}^{-1} \text{ yr}^{-1}$ if the crop is harvested during the grain filling period.

Schjoerring et al. (2000) represent a net source of NH_3 to the atmosphere below 1 up to $7 \text{ kg NH}_3\text{-N ha}^{-1} \text{ yr}^{-1}$ under field conditions. They further state that up to 5% of the shoot N content is lost as NH_3 if fertilizer or manure is applied (Holtan-Hartwig and Bockman, 1994).

With most of the information available on NH_3 losses conducted in northern Europe, annual loss values also represent a range of conditions reporting the largest NH_3 losses in temperate or midlatitude type of location, low humidity and cold temperatures. The high N losses from some crops are reported by Cerre and Gagianas (1991) and Fraaije and Gagianas (1991) as $1.5 \text{ kg NH}_3\text{-N ha}^{-1}$. The large N losses are however the number of studies is small and NH_3 is a rare phenomenon and that the losses are substantial. This increases the uncertainty of emissions from crops.

Temperature differences between northern Europe and northern Europe would be expected from crops grown in the USA. The temperature differences between Spring and Summer in the UK, two sites where numerous studies have been performed, there is typically a

the last 50 yr. Their explanation is the rapid reactions between atmospheric NH_3 and crop surfaces. These reactions have increased in the last 50 yr. Reactions decreasing atmospheric NH_3 from crop canopies.

NH_3 is generally within the range of 1–10 $\mu\text{g NH}_3\text{-N m}^{-3}$ (Holtan-Hartwig and Bockman, 1994). Compensation point for young plants is generally within the range of 1–10 $\mu\text{g NH}_3\text{-N m}^{-3}$. When the NH_3 concentration is $> 10 \mu\text{g NH}_3\text{-N m}^{-3}$, NH_3 may be taken up by plants. Morgan and Parton (1989) found that NH_3 concentration increases as plants approach maturity, to 23 $\mu\text{g NH}_3\text{-N m}^{-3}$ at grain filling, to 23 $\mu\text{g NH}_3\text{-N m}^{-3}$ at approximately a 10-fold increase in NH_3 concentration gradient between the leaves as the major driving force for

the supply of C in the form of 2-carboxylic acid cycle (Schroeder et al., 1991). Rates may also determine how utilization of N during the reproductive photosynthetic conditions (e.g., relative to C and result in NH_3 loss). Papakosta and Gagianas (1991) noted that grain yield for winter wheat reported similar findings that NH_3 grain N content and total shoot N when favorable climatic conditions) and effective deposition in the soil. Therefore, NH_3 emission will control C substrate production

Cultural Plants

Problems between air and crops can be problems estimating annual NH_3 emissions. Methods have difficulty matching the volatilization of NH_3 over temperature, wind speed, ambient humidity (Holtan-Hartwig and Bockman, 1994). Methods have problems with temperature and the requirement for uniform, directional vertical flux densities. Local micrometeorological techniques on plants, but give a combined

NH_3 flux from plants and soil. Standing N methods measure changes in total N quantity of aboveground plant parts at different developmental stages, but N losses can be masked by concurrent uptake of N by the roots. Standing N methods also cannot differentiate if N is lost as NH_3 or in other ways. Isotopic N has been used with standing N methods to evaluate N loss pathways, but isotope fractionation and substitution occurring during foliar emission and reabsorption cause problematic errors in estimating annual NH_3 emissions from plants (Francis et al., 1997; Harper and Sharpe, 1998).

The bidirectional nature of NH_3 exchange between plants and air along with the large spatial variability in ambient NH_3 concentrations and land use makes the extrapolation of current NH_3 exchange data to annual net NH_3 exchange on a landscape scale a speculative exercise. Holtan-Hartwig and Bockman, (1994) provide a comprehensive list of 50 references on volatile N losses from plants. The magnitude of N losses found by use of different measuring methods and for different plant species and developmental stages are listed in this review. Most of the reported studies are from cereal crops. In reviewing these studies Holtan-Hartwig and Bockman, (1994) found that emissions mostly fell in the range of 5 to 50 $\text{g NH}_3\text{-N ha}^{-1} \text{ d}^{-1}$, but concluded that daily emissions cannot be directly converted to yearly losses as emissions vary with conditions of temperature, water status and plant development stage. They suggest 1.5 $\text{kg NH}_3\text{-N ha}^{-1} \text{ yr}^{-1}$ as a rough estimate for net NH_3 losses from arable crops and that this value may increase to 6 $\text{kg NH}_3\text{-N ha}^{-1} \text{ yr}^{-1}$ if the crop is severely stressed by disease or adverse weather during the grain filling period.

Schjoerring et al. (2000) report that plant communities on arable cropland represent a net source of NH_3 to the atmosphere with net emissions ranging from below 1 up to 7 $\text{kg NH}_3\text{-N ha}^{-1} \text{ season}^{-1}$, depending on plant N status and climatic conditions. They further state that NH_3 emissions may lead to a significant loss of up to 5% of the shoot N content. Ammonia emission from crops is also increased if fertilizer or manure is applied in amounts that substantially exceed crop needs (Holtan-Hartwig and Bockman, 1994).

With most of the information on NH_3 emissions from crops coming from studies conducted in northern Europe on C_3 plants, the question becomes are these annual loss values also representative for warmer climates and C_4 plants? Studies reporting the largest NH_3 emissions from crops generally tend to have Mediterranean or midlatitude type climates. Above-average temperatures at the study location, low humidity and crops under high N status may have contributed to the high N losses from some of the studies in warmer climates, such as Papakosta and Gagianas (1991) and Francis et al. (1993) with calculated N losses over 75 $\text{kg NH}_3\text{-N ha}^{-1}$. The large N losses reported in these studies may be nontypical, however the number of studies reporting large N losses indicates that this is not a rare phenomenon and that under certain conditions NH_3 loss and exchange can be substantial. This increases the degree of uncertainty in estimating annual NH_3 emissions from crops.

Temperature differences during the summer months between central USA and northern Europe would suggest a greater opportunity for NH_3 emissions from crops grown in the USA. If one compares June, July, and August ambient air temperatures between Springfield, IL, and Copenhagen, Denmark, or Edinburgh, UK, two sites where numerous studies on NH_3 emissions from crops have been performed, there is typically over a 10°C difference in average daily temperatures.

If the higher U.S. temperatures are used in Husted and Schjoerring's (1996) calculations along with parameters that give Schjoerring's et al. (2000) net NH_3 emissions range, the estimated range for Springfield, IL, would be 1 to 25 kg $\text{NH}_3\text{-N ha}^{-1} \text{ yr}^{-1}$. Estimating annual NH_3 emissions from crops carries a substantial degree of uncertainty and will require considerable work to be done before we fully understand NH_3 exchange between crops and the atmosphere.

In addition to normal leaf and canopy cycling of NH_3 , soils and plant residues can act as sources and sinks for NH_3 , thereby increasing the complexity of determining net annual NH_3 exchange between agricultural crops and the atmosphere. Fertilizers and livestock husbandry are typically considered the major contributors of NH_3 to the atmosphere and plants nearly insignificant contributors. However, the sheer number of plants spread across the landscape and the bidirectional nature of NH_3 exchange between plants and air suggests plants play a crucial role in atmospheric NH_3 concentrations. In Hungary, Horvath and Sutton (1998) found no apparent decrease in atmospheric concentrations of NH_3 and NH_4^+ when pig and cattle numbers were reduced 49 and 47%, respectively, over a 10-yr period. Holtan-Hartwig and Bockman, (1994) expressed reservations about the possible occurrence of high seasonal emissions of NH_3 from crops, stating a loss of 15 kg $\text{NH}_3\text{-N ha}^{-1} \text{ yr}^{-1}$ from crops would represent about 30% of total NH_3 emissions from Western Europe. In some cases the assigning of NH_3 source may be just a matter of semantics. As an example, if application of fertilizer or manure exacerbates the loss of NH_3 from plants an argument can be made for either the plant or N supplying material as being the NH_3 source.

Emissions from Dead Agricultural Plants

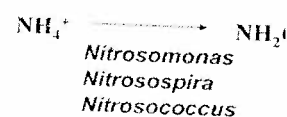
Decomposing plant material and herbage cut for hay, silage or mulch undoubtedly contributes to the emission of NH_3 to the atmosphere. Crop plants typically start senescence and dropping of lower leaves long before seed maturity is reached. Dropped leaves from crop species like oilseed rape may contain significant amounts of N, and high NH_3 emission can take place from such detached leaves with onset being synchronized with protein and chlorophyll degradation (Schjoerring et al., 1998). Nemitz et al. (2000) found the largest NH_3 concentration at the ground surface for a oilseed rape canopy and determined it was caused by N mineralization from fallen leaf litter that led to release of up to 150 ng $\text{NH}_3\text{-N m}^{-2} \text{ s}^{-1}$.

Janzen and McGinn (1991) found as much as 14% of the N in a legume green manure was volatilized as NH_3 within 14 d of application. Incorporation of green manure material into the soil effectively prevented volatile loss of NH_3 , but incorporation greatly reduces its effectiveness as a measure to control erosion and conserve moisture (Janzen and McGinn, 1991). Larsson et al. (1998) reported NH_3 losses from herbage mulch rich in N can be substantial with estimated losses ranging from the equivalent of 17% of the applied N for alfalfa (*Medicago sativa* L.) to 39% for high N grass.

Whitehead et al. (1988) measured the volatilization of NH_3 from cut herbage of perennial ryegrass (*Lolium perenne* L.) during a 70-d period of investigation for both drying and decomposition. They found NH_3 volatilization during decomposition amounted to 20 to 47% of the herbage N, but NH_3 volatilization during drying amounted to less than 1% of the herbage N. Most of the volatilization of NH_3 during decomposition occurred under moist conditions while the small amount of

□ Gaseous Losses other than

Nitrification



Main Controls

Substrate, O_2 , H_2O , T



Main Controls

Substrate, available C,

Fig. 8-1. Gaseous emissions (CC tems (Mosier and T. Parkin, 2007).

NH_3 volatilized during dry conditions is un head et al., 1988).

Nitrous Oxide and

Research during the past how NO_3^- and N_2O are prod lationships, and gas move me of processes involved we are of N that is applied or depos al., 2000; Del Grosso et al. (2 and Bouman, 1999; Potter et presumably similar agricultu in both time and space. The processes involved must be be developed (Mosier and B

We know that NO_3^- and processes of nitrification and Firestone, 1982; Hutchinson trification, the oxidation of a in essentially all terrestrial, logically ubiquitous, a surpri been identified and consider that occurs (Schmidt, 1982). water bacteria that oxidize at

ed and Schjoerring's (1996) calculating's et al. (2000) net NH_3 emissions, IL, would be 1 to 25 kg $\text{NH}_3\text{-N}$ crops carries a substantial degree risk to be done before we fully understand the atmosphere.

g of NH_3 , soils and plant residues increasing the complexity of determining agricultural crops and the atmosphere. y considered the major contributors insignificant contributors. However, the landscape and the bidirectional exchange suggests plants play a crucial role. Horvath and Sutton (1998) found emissions of NH_3 and NH_4^+ when pig manure, respectively, over a 10-yr period. Our reservations about the possible contribution of crops, stating a loss of 15 kg NH_3 about 30% of total NH_3 emissions. The origin of NH_3 source may be just a function of fertilizer or manure excretion. It can be made for either the plant or

Cultural Plants

for hay, silage or mulch undoubtedly contribute to the atmosphere. Crop plants typically release NH_3 before seed maturity is reached. Plants may contain significant amounts of NH_3 in such detached leaves with on-plant degradation (Schjoerring et al., 1996). NH_3 concentration at the ground surface it was caused by N mineralization of 10 ng $\text{NH}_3\text{-N m}^{-2} \text{ s}^{-1}$.

is 14% of the N in a legume green manure application. Incorporation of green manure reduced volatile loss of NH_3 , but in a field measure to control erosion and sedimentation, Larsson et al. (1998) reported NH_3 emissions with estimated losses ranging from alfalfa (*Medicago sativa* L.) to

ization of NH_3 from cut herbage over a 70-d period of investigation for NH_3 volatilization during decomposition. NH_3 volatilization during dry-down. Most of the volatilization of NH_3 occurs in the field while the small amount of

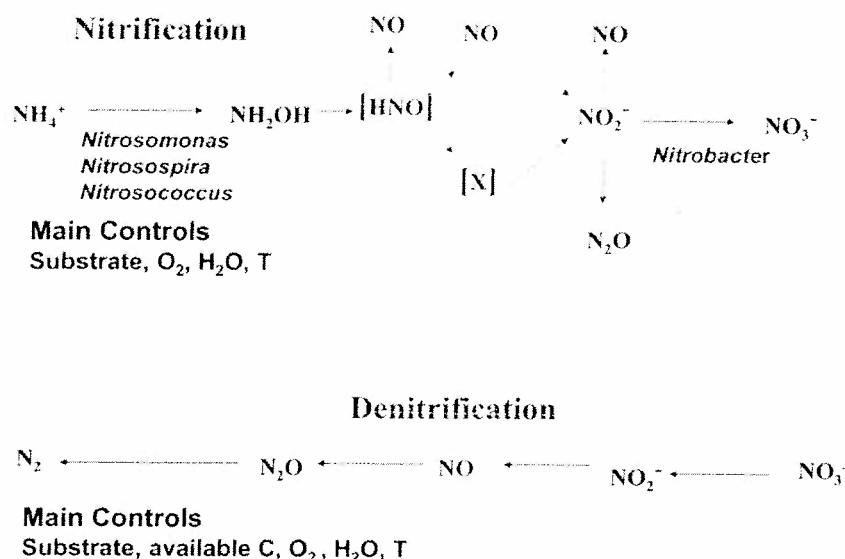


Fig. 8-1. Gaseous emissions (CO_2 , CH_4 , N_2O , and NO) from diverse agricultural production systems (Mosier and T. Parkin, 2007).

NH_3 volatilized during drying implies that hay made in the field under continuous drying conditions is unlikely to release appreciable amounts of NH_3 (Whitehead et al., 1988).

Nitrous Oxide and Nitrogen Oxides Biological Sources

Research during the past several decades has improved our understanding of how NO_x and N_2O are produced, factors that control production, source/sink relationships, and gas movement processes. However, despite extensive knowledge of processes involved we are only beginning to be able to predict the fate of a unit of N that is applied or deposited on a specific agricultural field (e.g., Davidson et al., 2000; Del Grosso et al. (2001a, 2001b; Frolking et al., 1998; Li et al., 1992; Plant and Bouman, 1999; Potter et al., 1998). Studies of emissions of NO_x and N_2O from presumably similar agricultural and natural systems show highly variable results in both time and space. The complex interaction of the physical and biological processes involved must be understood before reliable predictive capability can be developed (Mosier and Bouwman, 1993; Mosier et al., 1998a).

We know that NO_x and N_2O are produced primarily from the microbial processes of nitrification and denitrification in soil (Fig. 8-1) (see Schmidt, 1982; Firestone, 1982; Hutchinson and Davidson, 1993, for more detailed reviews). Nitrification, the oxidation of ammonia to nitrite and then nitrate (Fig. 8-1) occurs in essentially all terrestrial, aquatic and sedimentary ecosystems. Although ecologically ubiquitous, a surprisingly few different chemoautotrophic bacteria have been identified and considered to accomplish most of the ammonium oxidation that occurs (Schmidt, 1982). *Nitrosomonas* and *Nitrosospira* are the main soil and water bacteria that oxidize ammonia to nitrite while *Nitrobacter* is the principal ge-

nus of bacteria identified to oxidize nitrite to nitrate (Fig. 8-1; Schmidt, 1982). Denitrification, the microbial reduction of nitrate or nitrite to gaseous N through NO and N₂O (Firestone, 1982) (Fig. 8-1) is performed by a diverse and also widely distributed group of aerobic, heterotrophic bacteria that have the alternative capacity to reduce nitrogen oxides when O₂ becomes limiting. The general requirements for denitrification are: the presence of bacteria possessing the metabolic capacity, suitable electron donors such as organic C compounds, reduced S compounds or molecular hydrogen, anaerobic conditions or restricted oxygen availability, and nitrogen oxides as terminal electron acceptors (Fig. 8-1; Firestone, 1982).

In well-aerated, yet moist conditions, or approximately 60% water-filled-pore space (WFPS), N₂O and NO_x emissions from nitrification of ammonium-based fertilizers can be substantial (Bremner and Blackmer, 1978; Duxbury and McConaughy, 1986; Hutchinson and Brans, 1992). Other work suggests that N₂O release is a byproduct of nitrification (Yoshida and Alexander, 1970; Venterea and Rolston, 2002) and may occur by denitrification of nitrite by nitrifying organisms under oxygen stress (Poth and Focht, 1985). Nitric oxide emissions are considered to arise from the soil generally from nitrification (Hutchinson and Davidson, 1993) but can arise from abiotic chemical reactions under specific conditions (Nelson, 1982). In wet soils, where aeration is restricted, denitrification is generally the source of N₂O (Smith, 1990). Under these conditions both the rate of denitrification and the N₂O/(N₂ + N₂O) ratio must be known to evaluate N₂O emissions through denitrification. Typically little NO_x emissions are observed under such conditions (Hutchinson and Davidson, 1993). According to Smith (1990), soil structure and water content, which affect the balance between diffusive escape of N₂O and its further reduction to N₂, are important in determining the proportions of the two gases as well as NO_x. Soil WFPS is used to express the interplay of soil water content and microbial activity through most of these discussions, and is the one factor that is generally reflected in the response of trace gas emissions from the soil to changes in soil conditions. Linn and Doran (1984) showed that WFPS is closely related to soil microbial activity. As a result, the activity of soil microbial processes responsible for CH₄ production and consumption (Del Grosso et al., 2000a) and production and consumption of nitrogen oxides can be roughly predicted from WFPS (Davidson, 1991).

Linn and Doran (1984) demonstrated that aerobic microbial reactions, nitrification and respiration, peaked at WFPS of approximately 60% while responses that are sensitive to oxygen, i.e., denitrification, increased greatly above 80% WFPS. Firestone and Davidson (1989) developed the relationships of WFPS and soil microbial activity to describe NO and N₂O emissions. Their conceptual model, the hole-in-the-pipe (HIP) model, relates the sum of NO + N₂O emissions to indices of N availability and relates the ratio of NO/N₂O emissions to soil water content. The rates of nitrification and denitrification are described as being analogous to the flow of N through a pipe, while the sizes of the holes in the pipe determine the relative fractions of NO and N₂O that leak out. In fertile soils the flow through the pipe is large, and emissions of one or both gases are also large. In dry soils, NO is the dominant gas that leaks out of the pipe while in wetter soils N₂O is the more important endproduct (Davidson and Verchot, 2000; Davidson et al., 2000). Davidson (1991) observed that the largest NO emissions could be expected at WFPS values of 30 to 60% and the highest N₂O emissions at 50 to 80% WFPS.

□ Gaseous Losses other than

Under wetter soil conditions from the soil.

The interplay of substrate demonstrated by Parton et al. N₂O emissions from soils. The CENT ecosystem model (Davidson) consistently with observations from nitrification and denitrification that NO_x emissions are due to nitrification are proportional to function of modeled soil NH₄⁺. Nitrous oxide (N₂O) emission concentration, WFPS, heterotrophic activity, and soil moisture are calculated by multiplying to influence gas diffusivity. When diffusivity is low, denitrification is driven by nitrification with. When diffusivity is low, denitrification to less than one. The NO_x substrate by rain events onto dry soils.

Using the IPCC/UNEP/OECD estimates that the anthropogenic N₂O emission totaled 0.96 Tg in 1996 from fertilizer and biological N fixation residue. Anthropogenic NO_x emissions on Davidson and Kingerlee (1991).

Nitrogen Emissions

Most anthropogenic biomass estimates that nearly 87% of gas in the Tropics. Biomass burning economy (Andreae, 1991):

- Clearing of forest and brush
- Control of brush, weed lands;
- Nutrient regeneration in
- Control of fuel accumulations
- Production of charcoal for
- Energy production for co

In living plants the nutrients that are most easily burned, such as before burning, much plant tissue portion of its nutrients (Crutzen). contents of dry plant biomass are 0.01 to 0.3% P, and 0.5 to 3.4% I

Fig. 8-1; Schmidt, 1982). Denitrification is a diverse and also widely distributed process. The general requirements for denitrification are: (1) presence of nitrate, (2) reduced S compounds or reduced oxygen availability, and (3) absence of oxygen (Fig. 8-1; Firestone, 1982).

Approximately 60% water-filled-pore space is required for denitrification of ammonium-based fertilizers (Firestone, 1982; Duxbury and McConnell, 1978). Duxbury and McConnell's work suggests that N_2O release is a function of soil NH_4^+ concentration, soil moisture, soil temperature, pH, and soil texture. Nitrous oxide emissions are considered to be a function of soil NO_3^- concentration, soil moisture, soil temperature, pH, and soil texture. The NO_3^- emissions are calculated by multiplying total N_2O emissions by a NO_3^-/N_2O ratio function that is calculated as a function of soil parameters (bulk density, field capacity, WPFS) that influence gas diffusivity. When soil gas diffusivity is high most of the N gas flux is driven by nitrification with a correspondingly high NO_3^-/N_2O (maximum of 25). When diffusivity is low, denitrification dominates and the ratio of NO_3^-/N_2O drops to less than one. The NO_3^- submodel also simulates NO_3^- emission pulses initiated by rain events onto dry soils.

Using the IPCC/UNEP/OECD/IEA (1997) guidelines, USEPA (2001) estimated that the anthropogenic N_2O emissions from U.S. soils due to agricultural soil management totaled 0.96 Tg in 1999. This estimate is based on N input from synthetic fertilizer and biological N fixation as well as N recycled in livestock manure and crop residue. Anthropogenic NO_3^- emissions due to agricultural soil management, based on Davidson and Kinglerlee (1997), were an estimated 0.2 Tg of NO_3^- -N in 1999.

Under wetter soil conditions N_2 should be the dominant gaseous N product emitted from the soil.

The interplay of substrate availability, oxygen supply, and gas diffusion are demonstrated by Parton et al. (2002) who describe a model to simulate NO_3^- and N_2O emissions from soils. They have developed N gas flux modules for the DAYCENT ecosystem model (Del Grosso et al., 2006) and have tested the model extensively with observations from different soils. The N gas flux model assumes that nitrification and denitrification both contribute to N_2O and NO_3^- gas emissions but that NO_3^- emissions are due mainly to nitrification. Nitrous oxide (N_2O) emissions from nitrification are proportional to nitrification rates, which are calculated as a function of modeled soil NH_4^+ concentration, WPFS, temperature, pH, and texture. Nitrous oxide (N_2O) emissions from denitrification are a function of soil NO_3^- concentration, WPFS, heterotrophic respiration, and texture. The NO_3^- emissions are calculated by multiplying total N_2O emissions by a NO_3^-/N_2O ratio function that is calculated as a function of soil parameters (bulk density, field capacity, WPFS) that influence gas diffusivity. When soil gas diffusivity is high most of the N gas flux is driven by nitrification with a correspondingly high NO_3^-/N_2O (maximum of 25). When diffusivity is low, denitrification dominates and the ratio of NO_3^-/N_2O drops to less than one. The NO_3^- submodel also simulates NO_3^- emission pulses initiated by rain events onto dry soils.

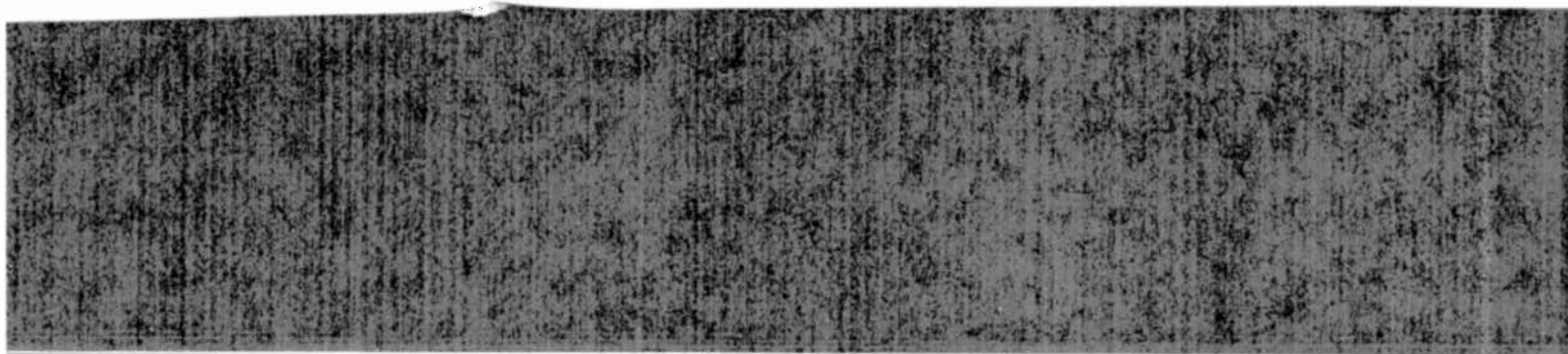
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Nitrogen Emissions from Burning Agricultural Biomass

Most anthropogenic biomass burning occurs in the Tropics. Andreae (1991) estimates that nearly 87% of global emissions from biomass burning takes place in the Tropics. Biomass burning serves a variety of purposes in agriculture and economy (Andreae, 1991):

- Clearing of forest and brush land for agricultural use;
- Control of brush, weeds, and litter accumulation on grazing and crop lands;
- Nutrient regeneration in grazing and crop lands;
- Control of fuel accumulation in forests;
- Production of charcoal for industrial and domestic use; and
- Energy production for cooking and heating.

In living plants the nutrients N and S are mainly concentrated in those parts that are most easily burned, such as leaves, small twigs and bark, but fortunately before burning much plant tissue is dry and dead and has actually lost a major portion of its nutrients (Crutzen et al., 1979). On a mass basis, the nutrient element contents of dry plant biomass are relatively low: about 0.3 to 3.8% N , 0.1 to 0.9% S , 0.01 to 0.3% P , and 0.5 to 3.4% K (Andreae, 1991).



Fires in diverse ecosystems are very different in the production of gaseous and particulate emissions (Levine et al., 1995). The chemical composition of emissions from burning biomass depends primarily on the rate of energy release (intensity) or combustion (Cofer et al., 1991a). Combustion is strongly coupled to fuel moisture, fuel type, fuel size, fuel array, ignition pattern, terrain, and weather. Flaming combustion produces more highly oxidized products such as CO_2 and NO , while smoldering leads to increased emissions of more reduced species such as CO , CH_4 , and NH_3 (Griffith et al., 1991). In open burning of biomass, temperatures are fairly low and the high temperatures necessary for the oxidation of atmospheric N seldom exists (Gerstle and Kemnitz, 1967).

Nitrogen is present in plant biomass mostly as amino groups (R-NH_2) in the amino acids of proteins (Andreae, 1991). During combustion it is released by pyrolytic decomposition of the OM and then partially or completely oxidized to various volatile N compounds. On average approximately 90% of the biomass N is volatilized during a burn (Lobert et al., 1990). Nitric oxide is the single most abundant species emitted, but it represents only 10 to 20% of the N initially contained in the fuel (Andreae, 1991). Clements and McMahon (1980) reported a similar amount with a rough average of about 30% total yield for all NO_x species. Nitrogen compounds other than NO (NO_2 , N_2O , NH_3 , HCN , organic nitriles, and nitrates) account for another 10 to 20% of the fuel N (Andreae, 1991). Average emission values reported by Lobert et al. (1990) for percentage of biomass N released as NH_3 , HCN , and nitriles of 4, 2.4, and 1% respectively, lie well within this range. Emission of molecular N usually is not monitored because of its high atmospheric content, and the majority of any unaccounted-for N is possibly released as N_2 (Andreae, 1991). Lobert et al. (1991) using a burning apparatus with an artificial atmosphere for simulating open fires reported 41 to 46% of the fuel N was emitted as N_2 . They concluded N_2 emissions belonged to the flaming stage rather than to the smoldering stage.

LeBel et al. (1991) estimated NH_3 emissions from biomass burning would account for 14% of the total global atmospheric NH_3 budget. This is much higher than the Lobert et al. (1991) estimate that shows biomass burning on average accounting for about 5% of the total NH_3 source. In nearly all of their experiments, Lobert et al. (1991) found NO_x to be the most important reactive N emission product from biomass burning and from their calculations of source strength yields estimated an average contribution of 12% to the global budget. This falls in the range of 10 to 20% of the global NO_x budget estimated by Granier et al. (2000) for NO_x from biomass burning. For N_2O , Cofer et al. (1991b) concluded that no more than 7% (and probably less) of the global source of N_2O can be attributed directly to biomass burning. Similarly, Lobert et al. (1991) estimated biomass burning contributing only about 3% to the global source of N_2O . Lobert et al. (1991) reported that HCN and CH_3CN , two of the most important nitriles emitted by biomass burning, together released 3.6% of the fuel N and in some experiments, HCN emissions can be as high as NO_x emissions when incomplete combustion was predominant. Data on global sources of nitriles is lacking, however biomass burning may well be the major source for the release of these gases into the atmosphere Lobert et al. (1991).

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in the production of gaseous and chemical composition of emissions rate of energy release (intensity) is strongly coupled to fuel moisture, terrain, and weather. Flaming fuels such as CO_2 and NO , while reduced species such as CO , CH_4 , biomass, temperatures are fairly oxidation of atmospheric N sel-

as amino groups (R-NH_2) in during combustion it is released by partially or completely oxidized to approximately 90% of the biomass N. Nitric oxide is the single most 10 to 20% of the N initially consumed. McMahon (1980) reported a similar yield for all NO_x species. NH_3 , HCN , organic nitriles, and fuel N (Andreae, 1991). Average for percentage of biomass N released respectively, lie well within this monitored because of its high atmospheric-for N is possibly released as burning apparatus with an artificial to 46% of the fuel N was emitted the flaming stage rather than to

from biomass burning would account budget. This is much higher than biomass burning on average accounting all of their experiments, Lobert et al. reactive N emission product from source strength yields estimated at 10. This falls in the range of 10 to 20% (Cramer et al. (2000) for NO_x from biomass that no more than 7% (and attributed directly to biomass burning, biomass burning contributing only about 10%) reported that HCN and CH_3CN , biomass burning, together released 10% emissions can be as high as NO_x dominant. Data on global sources likely will be the major source for the (Cramer et al. (1991).

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